Laboratory activities related to marine corrosion: search for damage causes

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- **INTRODUCTION TO SEA-WATER CORROSION PHENOMENA**

- **CASES OF STUDY**

  - ❑ *Galvanic corrosion phenomena produced by the contact between aluminium alloy casting (pump lever) and copper alloy casting (thermostatic valve) installed on the main engine's cooling system.*

  - ❑ *Stainless steel welded joints of the sea-water cooling system affected by macroscopic weld defects which promoted corrosion phenomena and main system dysfunction.*

  - ❑ *Propeller shafts realized by precipitation hardening martensitic stainless steel (17-4 PH) subjected to a diffused pitting and crevice corrosion phenomena.*

  - ❑ *Sea-water cooling intake system realized in carbon steel affected by crater-form corrosion due to lack of adequate protection and galvanic contact with stainless steel in shoreline conditions.*

  - ❑ *Crevice corrosion on welded joints of an aluminum alloy hull.*

INTRODUCTION TO SEA-WATER CORROSION PHENOMENA

Seawater can be schematized as a dynamic system, consisting of an aqueous solution of salts, gases, organic and living compounds as well as insoluble particles.

MAIN VARIABLES GOVERNING THE PHENOMENA

- **temperature**
- **salinity**
- **systems interacting in the oxygen production**
- **sites (coastal or open water)**

Is then absolutely important having solid references of basic case histories to which refer in order to better understand the seawater environment, its effects on metallic and non-metallic structures and the whole of the best practices in terms of protection of the structure and corrosion prevention.

Due to the many variables which may affect the corrosion process several different types of corrosion may occur. The most useful and the one to which generally refer is the classification according to the appearance of the phenomenon, according to which is possible make a reasonable distinction

Uniform attack,
generally acting over large surfaces thanks to an homogeneously distributed anodic and cathodic process over the metal surfaces, guaranteed by a system which exhibits no major heterogeneities, either in the metal composition, in the environment or in the exposure conditions.

Localized corrosion,

- galvanic and contact corrosion
- pitting phenomenon
- crevice corrosion
- flow induced corrosion
- intergranular corrosion
- stress corrosion

Selective corrosion,
also called selective leaching or parting in which one element of a metallic compound is selectively removed from the alloy's matrix.

Case 1 - Galvanic corrosion phenomenon

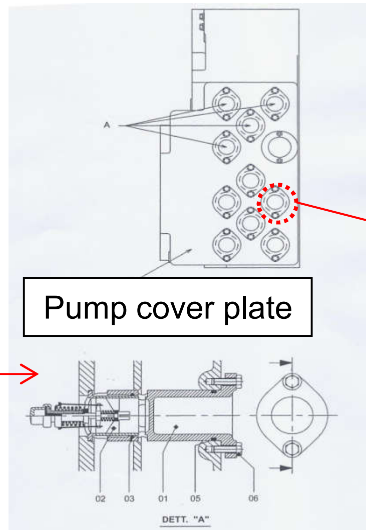
Environmental exposure and structure materials and generalities

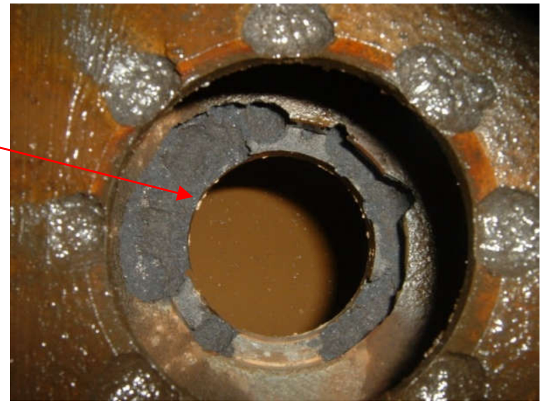
The corrosion phenomena occurred in each of the four cases at the section of the pumping system between the aluminum alloy (**GAlSi9MnMg**) cover plate of the pump lever and the copper alloy thermostatic valve (**GCuSn5Zn5**), which is regulating the cooling liquid flowing to the main engine.

Structure superficial appearance

The corrosion phenomenon documented on board of the four vessels has been localised in two main positions

- Contact position between the aluminum cover plate and the thermostatic copper alloy valve
- Portions of the recirculation cooling system where the light alloy components were close to recirculation pumps realized in cast iron





Case 1 - Galvanic corrosion phenomenon

Laboratory tests and exams

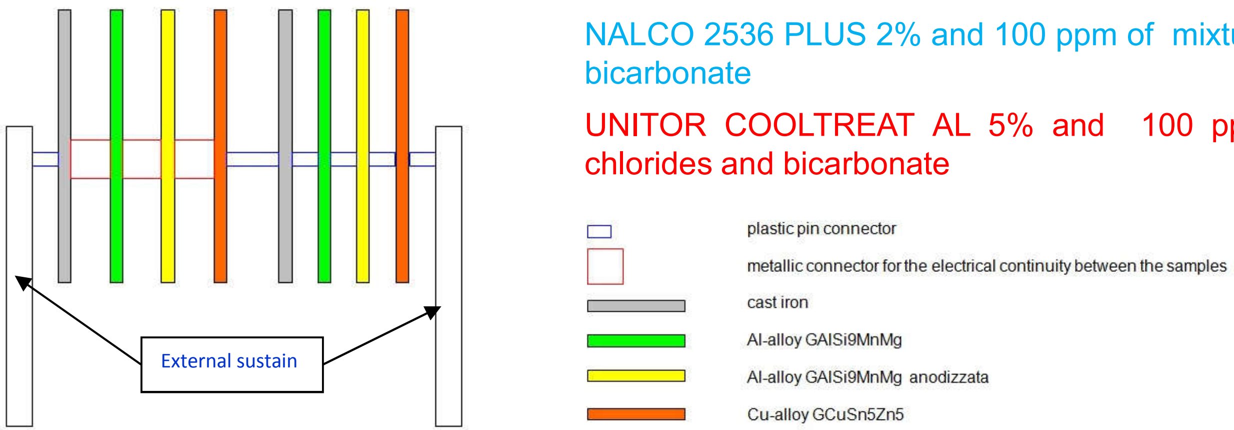
- Inductively coupled plasma atomic emission spectroscopy (ICP-AES) ➡ Conducted on 5 cooling water samplings, addicted with anticorrosion product adopted on-board, inspecting for metallic particles or intermetallic compounds ascribable to possible causes of the documented damages

- Comparison of two protective additives (NALCO 2536 plus – UNITOR COOLTREAT AL) used in the cooling system simulating operating on board conditions and evaluating the corrosion rate on the tested samples according to ASTM D1384 – 05 (Standard Test Method for corrosion test for engine coolants)

➡ Tested solutions @ 88 ± 2°C, with 100 ± 10 ml/min of aeration for 336 hrs

NALCO 2536 PLUS 2% and 100 ppm of mixture of sulphate, chlorides and bicarbonate

UNITOR COOLTREAT AL 5% and 100 ppm of mixture of sulphate, chlorides and bicarbonate



Case 1 - Galvanic corrosion phenomenon

Results and Observations

After the corrosion tests

- None of the tested samples presented a macroscopic corrosive attack such as the components installed on board.
- Weight losses happened to slightly differ between the samples exposed in the cells where the liquid solutions were continuously mixed and those submerged in the still liquid solutions
- For any of the testing conditions the additive UNITOR COOLTREAT AL happened to be slightly more successful in guarantying a lower weight loss

The investigated corrosive attack was definitely enhanced and accelerated by the direct contact of materials defined by extremely different electrochemical potentials. On the top of it the Al light alloy typically suffer of crevice corrosion phenomenon, in position where the aeration is then strictly reduced, as for the corroded components installed by the recirculation pumps.

Recommended solution ➡ **Substitution of Al-alloy, implementation of proper isolating system**

Case 2 – Corrosion phenomenon on stainless steel welded pipes

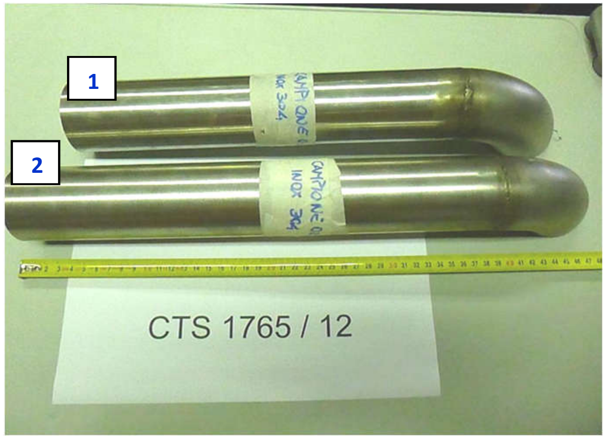
Environmental exposure and structure materials and generalities

On a 12 meters boat realized in the Aluminum alloy – **EN AW 5083** – equipped with a cooling system of **AISI 304** sea water fed, few months after the delivery, during which the usage of the craft was declared as minimum, leakages were detected on the piping, mainly located by welding positions.

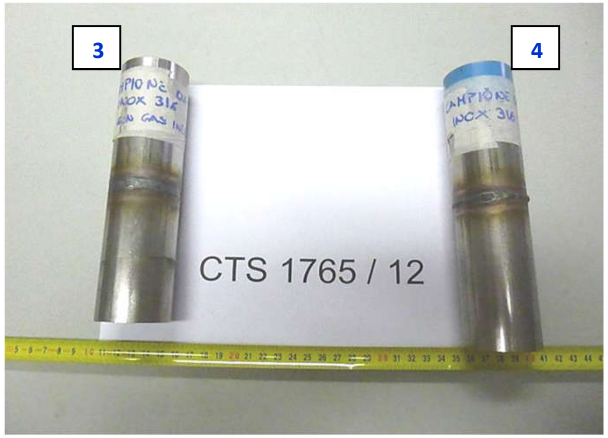
Structure superficial appearance

Two different sampling have been tested and examined, one of **AISI 304L** mounted and assembled onboard and one **AISI 316L** realized as prototype by shipyard as possible repairing of the cooling system.

AISI 304L samplings from the onboard installation



AISI 316L samplings from the proposed repairing



Case 2 – Corrosion phenomenon on stainless steel welded pipes

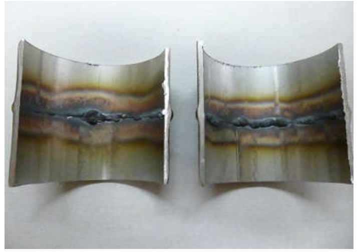
Laboratory tests and exams

Visual external inspection

Macrographic examination

Conducted on the on-board installed pipes were focused in the detailed description of the **corrosion morphology** and **surfaces and joints general conditions**

On the samplings proposed as repairing the attention was focused on the evaluation of the realized welds, determining **unacceptable operating defects of the joining**



Chemical analysis

Sample N°	C (%)	Si (%)	Mn (%)	P (%)	S (%)	Cr (%)	Ni (%)	Mo (%)
1	0,0227	0,471	1,66	0,0295	0,0005	18,29	8,65	0,31
2	0,0276	0,438	1,77	0,0274	0,0005	18,13	8,81	0,22
3	0,0170	0,459	1,70	0,0358	0,0019	17,46	10,59	2,10
4	0,0256	0,466	1,64	0,0271	0,0012	17,27	10,34	2,15

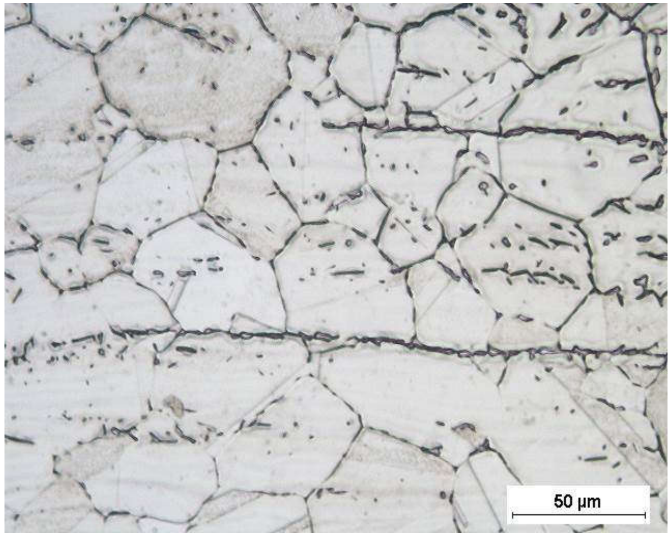
ASTM A312 Standard Specification for Seamless, Welded, and Heavily Cold Worked Austenitic Stainless Steel Pipes (2017)

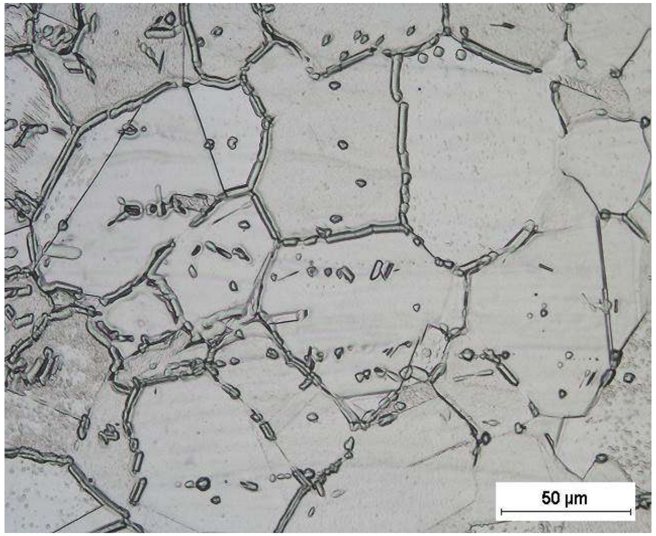
Case 2 – Corrosion phenomenon on stainless steel welded pipes

Laboratory tests and exams

Micrographic examination

Samples number 3 and 4 (AISI 316L) have been prepared in order to inspect the microstructure, specifically focusing on positions close to the welding joints.





➡ In these areas, especially in the heat affected zones, was clearly evident a **diffused precipitation of carbides at the grain boundaries** so to characterize the consequent **sensitization phenomenon** enhancing the intergranular corrosion chances

Case 2 – Corrosion phenomenon on stainless steel welded pipes

Results and Observations

On-board installed components ➡ Appeared affected by severe localized pitting corrosion attack close to the longitudinal welding as well as a more diffused phenomenon, generally observed on a the lower internal surface of the pipes, where conditions such as stagnant coolant and corrosion deposits may have enhanced the corrosion rate.

Proposed substituting components ➡ Characterized by serious welding operating defects, like the lack of penetration and fusion as the improper backing gas protection and the heat tint colour, due to an incorrect setting of the welding parameters. This conditions induced a geometrical non-uniformity and the precipitation of carbides, both responsible for the eventual reduction of the corrosion resistance of the material.

- This case of failure highlights how key factors for the corrosion resistance of any structure are not only related to the **most suitable and proper materials** for the specific applications but also to mostly define **correct**, **adapted** and **verified welding procedures** realized by **qualified welders**.

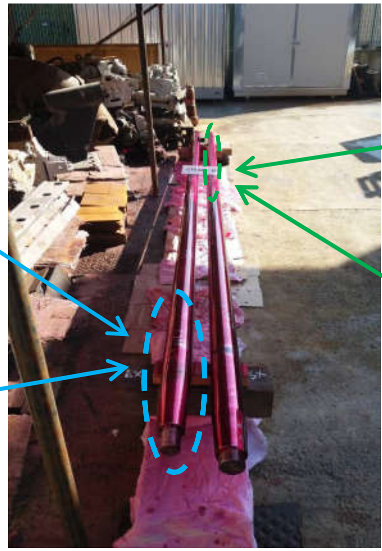
Case 3 – Pitting and crevice corrosion event

Environmental exposure and structure materials and generalities

This case refer to the corrosion phenomena detected on the propeller shafts, 95 mm in diameter realized in precipitation hardening martensitic stainless steel: **17- 4 PH** (**ASTM A564 – 13 Type 630 – UNS 17400**)

Structure superficial appearance

The two shafts appeared affected by both **localized pitting** corrosion phenomena and **crevice** one. Considering the technical description of the engine on-board installation, the most of the corrosion attack was observed corresponding to the **inboard portion** of both the components.



Case 3 – Pitting and crevice corrosion event

Laboratory tests and exams

Visual external inspection
Dye penetrant test

➡ Tests were conducted with the main objective of precisely define the disposition of the major damages caused by the corrosion attack, to better and more successfully localize further detailed investigation.

Chemical analysis
Mechanical test

➡ To define the chemical composition and mechanical properties declared by the material's certificate.

Checked positions	C (%)	Mn (%)	P (%)	S (%)	Si (%)	Cr (%)	Ni (%)	Cu (%)	Nb+Ta (%)
Surface	0.053	0.43	0.026	0.0023	0.36	15.16	4.46	3.76	0.35
Section	0.051	0.41	0.023	0.0023	0.36	15.34	4.43	3.57	0.32
Reference values ASTM A 564 - 13 Type 630 H 1150	**0.07 max**	**1.0 max**	**0.040 max**	**0.030 max**	**1.0 max**	**15.0 - 17.5**	**3.0 - 6.0**	**3.0 - 6.0**	**0.15 - 0.45**

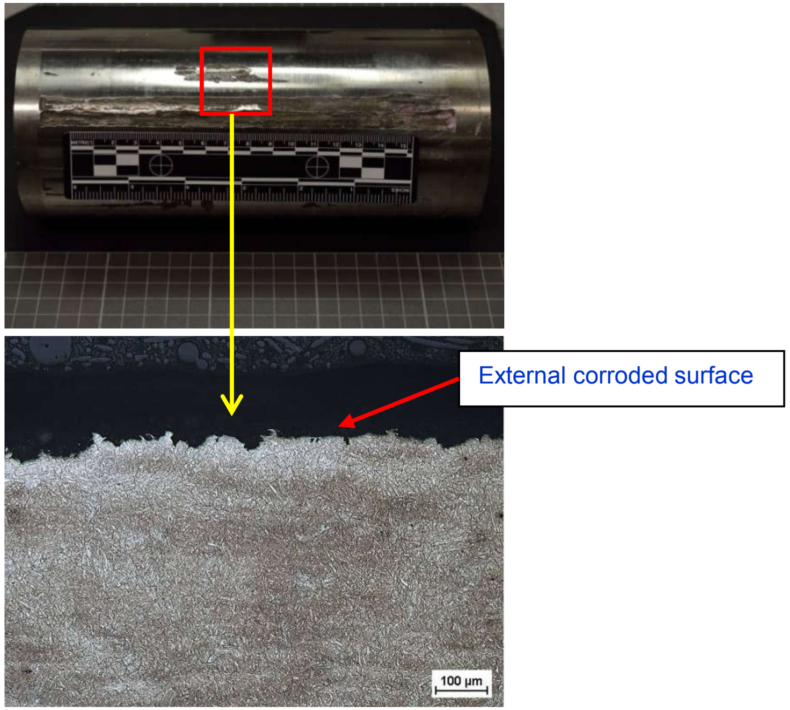
Sample	Rm (MPa)	Rp0,2 (MPa)	A (%)	Z (%)	HB	KV (J)
Port-side shaft	976	785	22,5	58.9	323	148
Reference values ASTM A 564 - 13 Type 630 H1150	**930 min**	**725 min**	**16 min**	**50 min**	**277 min**	**41 min**

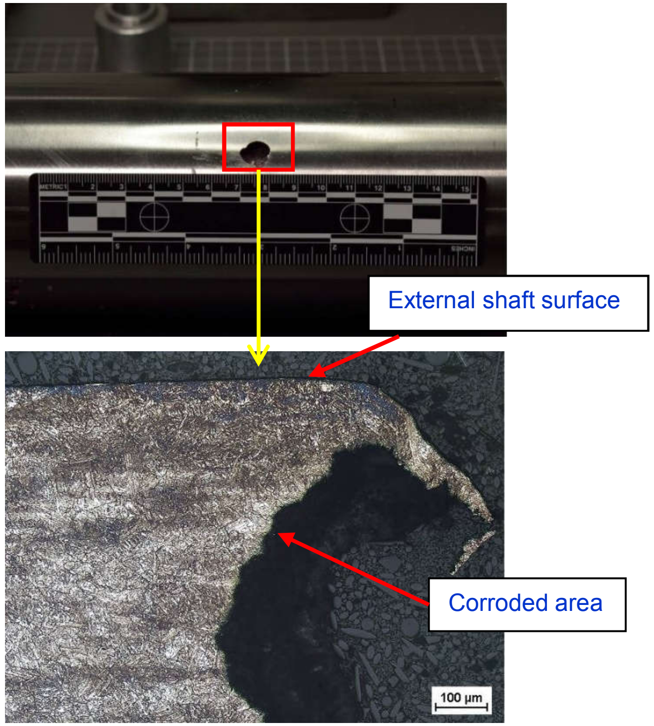
Case 3 – Pitting and crevice corrosion event

Laboratory tests and exams

Micrographic investigation

➡ The surfaces morphologies of two specifically identified sections, one on a corrosion pit and the other on a crevice affected zone, have been inspected to better determine and check the metallurgical state of the material.





Case 3 – Pitting and crevice corrosion event

Results and Observations

The observed and examined corrosion phenomena are strictly correlated to the specific service and the typical exposure and operating conditions.
The martensitic stainless steel 17- 4PH, as generally all the stainless steel, suffers **severe crevice corrosion effects** in case of **scarce aeration** and particularly when the **component** is kept **steady in stagnant liquid** and a thin liquid layer is preventing its natural passivation process.

Recommended solution ➡ **Periodical rotation and motion of the shafts**
Adequate and supplementary prevention system

Case 4 – Crater-form corrosion

Environmental exposure and structure materials and generalities

In this specific case the failure occurred onto the sea water cooling system of a private motor yacht.

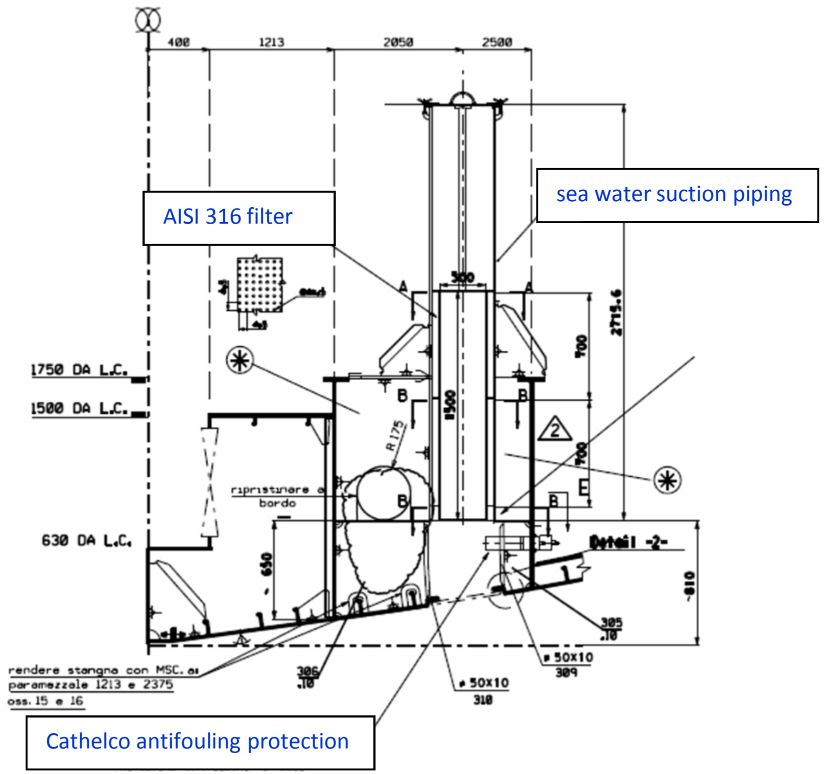
Corrosion protection system

- The hull was protected by **fourteen zinc alloy sacrificial bolted type anodes** (10,8 kg; 455x100x45 mm) on each side, four anodes (idem) on stern, one circular zinc bolted anode on each rudder and one cone shaped zinc anode on each of the two propeller shaft

- In the sea water cooling piping, the antifouling protection was provided by a **Cathelco impressed current system**

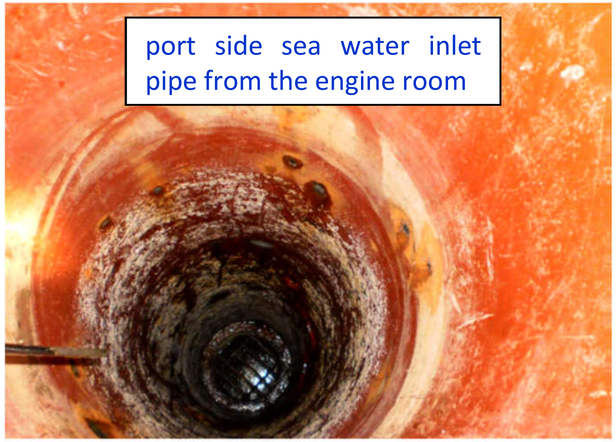
- **Iron anodes**, inside the copper-nickel pipes, provides cathodic protection of the copper-nickel alloy

- The copper-nickel pipeline is separated from the carbon steel pipe by an austenitic **stainless steel hub** declared AISI 316L



Case 4 – Crater-form corrosion

Structure superficial appearance



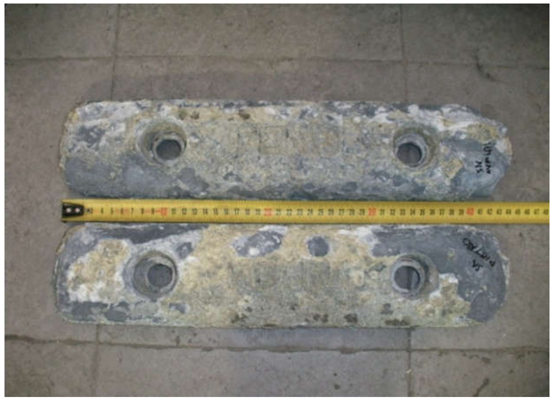
The anodes were electrically connected to the hull, as tested with ASITA MD533 tester. The portion of oxide and fouling scale wasn't conductive. The on board equipment on engine room were generally electrically grounded to the hull. In particular a wiring connection was realized between the main electric box and all the flanges of cooling systems were connected with copper plate.

Case 4 – Crater-form corrosion

Laboratory tests and exams

- The six different portions of the sea water piping have been visually examined and the crater shaped pitting holes were dimensioned and documented, as well as the conditions of the sampled zinc anodes

- Portion of the pipe dedicated to the sampling for chemical, mechanical and microstructure analysis



Case 4 – Crater-form corrosion

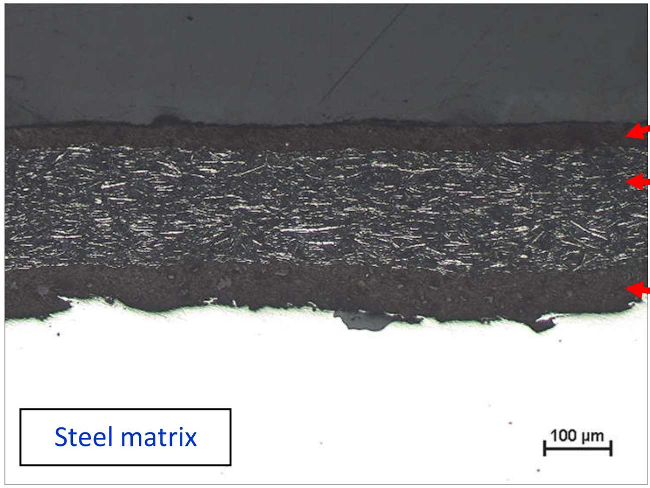
Laboratory tests and exams

Chemical analysis - AES
Mechanical test

The chemical composition matched the requirements as reported by the requirement prescriptions for a carbon steel type **Grade 460 Chapter 6 "Lloyd's Register Rules for the manufacture, testing and certification of materials"**. Same conclusion have been confirmed by mechanical tests carried out on specimens sampled from same pipe as for the chemical examination.

Microstructure examination

On the internal surface was documented three different paint layers
The **first layer** is the one directly in contact with the steel (**57µm**) which is the **shop primer**, the **second** one (**188µm**) which is corresponding to the **zinc reach barrier coating** then the **last coating level** is the outer one (32µm) and ascribable to the **red primer** finishing deposition



Case 4 – Crater-form corrosion

Results and Observations

- The pipes were realized with a Grade 460 C – Mn steel.
- The paint barrier on the inner side of pipe was about 127 μm
- The chemical composition of zinc anodes was according to the standard
- The sacrifiical anodes were in any case able to shift the hull potential under - 800mV giving full protection in aerated sea water
- The Chatelco antifouling system provide second negative potential shift but not enough to reach the full protection for anaerobic sea water condition
- A major extension of oxides and fouling on anodes was probably a limiting factor of the adequate efficency of the cathodic system

On the basis of the obtained results the most probable corrosion scenario was a **poor protection of the steel** (locally poor paint film, poor cathodic protection in the higher pipe portion), **stagnant condition** (may be anaerobic) and the **presence of a large stainless steel cathodic area** (the filter section) that induced a galvanic corrosion phenomenon localized on little anodic areas, portion of the hull where vacancies of the paint layers were highlighted, reducing the overall corrosion resistance of the structure.

Recommended solution

Realization of a good paint substrate
Proper cathodic protection on the higher pipe portion
Eliminate the electrical connection between stainless steel filters and the mild steel piping

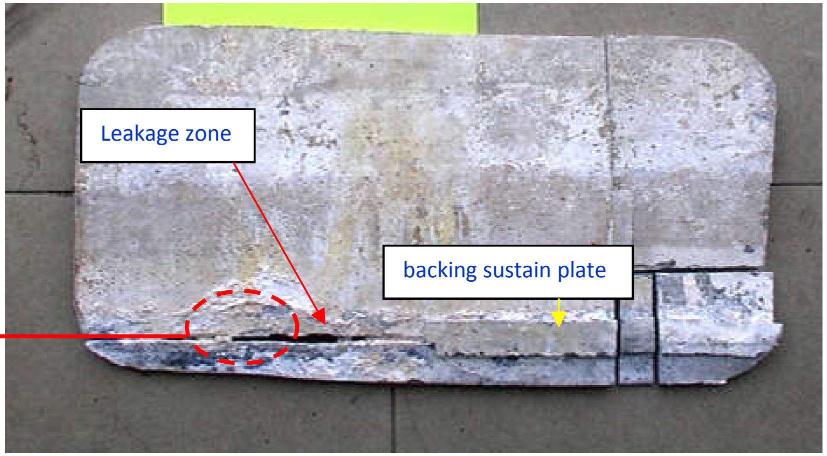
Case 5 – Crevice corrosion on welded joints

Environmental exposure and structure materials and generalities

Object of this case review are the laboratory analysis conducted on damages observed localized at the hull's bow of a private sailing yacht. In this position a severe water leakage was detected and after consequent on site inspection, for the replacing of the damaged hull's plate, the whole ballast tank was flooded and covered in a gelatinous whitish sludge and solid deposits.

Structure superficial appearance

The hull's plate appeared seriously deteriorated. Close to the weld position were observed diffused and clear **evidences of white and grey solid deposits** fully resembling Al oxides



Case 5 – Crevice corrosion on welded joints

Laboratory tests and exams

Chemical analysis

Results from the atomic absorption and gravimetric analysis confirm the overall matching of the chemical compositions concerning the sampled sludge and the solid deposits dispersed over the inner surface of the plate, mainly characterized by Al-oxide and Mg-oxide

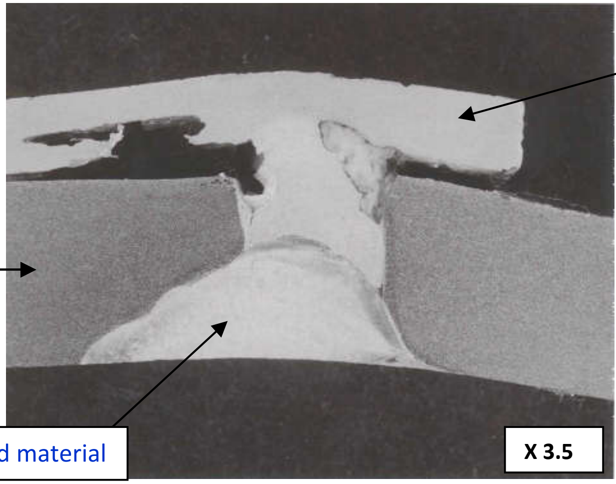
sample	Si %	Fe %	Cu %	Mn %	Mg %	Cr %	Zn %	Ti %
Hull's plate	0,18	0,40	0,092	0,26	2,69	0,035	0,038	0,012
Backing plate	0,07	0,28	0,064	0,51	4,46	0,089	0,091	0,009
Weld metal	0,08	0,24	0,028	0,46	3,92	0,073	-	-

The chemical composition by AES of the **hull's plate** matched the specified requirements as indicated in the applicable reference standard **IACS W25 - type 5754**, while the **backing plate** corresponded to the type 5083, as specified in the same reference document. Concerning the weld metal the chemical composition resembled the one of the **filler metal ER5183** according to AWS A 5.10 standard

Case 5 – Crevice corrosion on welded joints

Laboratory tests and exams

Macrografic examination



Corrosion phenomenon enhancer, being responsible of important **crevice attack** localized on the **HAZ**

Results and Observations

Light alloy metallurgically suffer **operating conditions and geometrical applications in which a proper aeration is not ensured**. In case of rupture or damaging of the natural self protecting oxide layer and being impeded its natural restoring process (lack of proper oxygen concentration flow) the material is then openly prone to corrosion attack. In the specific case the severe sea water leakage through the hull's damaged plate, combined with the extremely limited aeration conditions of the failed section (ballast tank) induced the generation of an highly aggressive environment for the Al-alloy structure.

THANK YOU FOR THE ATTENTION